Conductivity and Hall Effect in the Intrinsic Range of Germanium

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Conductivity and Hall effect have been measured in the intrinsic range of germanium from 250° to 1000°K. From lattice-scattering mobility and conductivity below 500°K, a new empirical expression for carrier concentration is determined: $np=3.10\times10^{32}T^3\exp(-0.785/kT)$. An estimate is made of the contribution of optical modes to the lattice-scattering mobility. Conductivity from 500° to 1000° and Hall effect from 250° to 1000° are computed and compared with experiment. Included in the computation are: the empirical expression for carrier concentration modified by the change in intrinsic ionization energy produced by electrostatic interaction of charge carriers, extrapolated empirical lattice scattering mobility, scattering by electron-hole collisions, and an extrapolation of the ratio Hall mobility/conductivity mobility.

1. INTRODUCTION

EFFORTS to understand the semiconducting properties of germanium have been confined for the most part to the range of impurity conductivity; literature on the intrinsic range is meager. Theory is incomplete, but enough is known to say that the number of processes involved in conduction are too numerous to be separated empirically from measurements of conductivity and Hall effect. This paper, therefore, is not a complete analysis of the intrinsic range but tries to indicate the relative importance of some of the conduction processes by comparing experiment with available theory.

Conductivity and Hall effect in the intrinsic range of germanium are reported for the temperature range 250° to 1000° Kelvin. The data are analyzed in two steps, the results below 500°K being considered first. It is believed that below 500° the conduction mechanism contains fewer unknowns and that a reliable expression for carrier concentration can be obtained from conductivity and lattice-scattering mobility. The temperature dependence of lattice-scattering mobility has been determined[1] from 100° to 300°K and found to deviate from the $T^{-1.5}$ law predicted by theory. It is shown that all of the deviation found for electrons and some of the deviation found for holes can be accounted for by assuming the presence of optical mode scattering. Most of the deviation from the $T^{-1.5}$ law found for holes may arise because the band edge is not at the center of the Brillouin zone. However, when the carriers have gained enough thermal energy, this scattering mechanism will have a $T^{-1.5}$ temperature dependence and acoustical mode scattering can be expected to return to the $T^{-1.5}$ law at some temperature above 300°K. Since this temperature is not known, the effect has been neglected and measured lattice scattering mobility is extrapolated from 300° to 1000°K. From lattice-scattering mobility and conductivity below 500° an empirical expression for carrier concentration is determined.

Conductivity above 500° is computed and compared with experiment. Included in the computation are the empirical expression for carrier concentration modified by the change in intrinsic ionization energy produced by electrostatic interaction of charge carriers; extrapolated lattice-scattering mobility; and scattering by electron-hole collisions. Hall effect from 250° to 1000° is computed and compared with experiment, making use of information obtained in computing conductivity plus an extrapolation of the ratio: Hall mobility/conductivity mobility. This ratio has been determined between 100° and 300° and found for holes to be increasing with temperature above the theoretically predicted constant 1.18. Along with the departure from the $T^{-1.5}$ law, this effect is expected to disappear at some temperature above 300° and the ratio to decrease to some constant value. Since the actual behavior of the ratio has not been determined, a linear extrapolation of the measured ratio from 300° to 1000°K is used in computing the Hall coefficient. Computed conductivity and Hall effect agree well with experiment. This is encouraging in view of the large number of assumptions made in the analysis.

2. METHODS

Conductivity and Hall effect were measured on bridge shape[2] samples having rhodium plated contact areas. All samples were cut from recently grown single crystal germanium. Measurements above 350°K were made using a ceramic holder fitted with pressure contacts of platinum 10 percent rhodium wire and platinum-platinum 10 percent rhodium couples. Samples were heated in a small electric furnace and an atmosphere of nitrogen.

3. SYMBOLS

σ = conductivity in $\text{ohm}^{-1}\,\text{cm}^{-1}$,
R_H = Hall coefficient in cm^3/coulomb,
n, p = electron and hole concentration in cm^{-3},
n_i, p_i = carrier concentration when all impurities are ionized (the difference between donor and acceptor concentration),
μ_{cn}, μ_{cp} = electron and hole conductivity mobility in cm^2/volt sec,

[1] F. J. Morin, Phys. Rev. **93**, 62 (1954).

[2] P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693–706 (1954).

μ_{Ln}, μ_{Lp} = electron and hole lattice scattering mobility,
μ_{Hn}, μ_{Hp} = electron and hole Hall mobility,
μ_{ac} = lattice-scattering mobility acoustical modes,
μ_{op} = lattice-scattering mobility optical modes,
μ_{np} = electron-hole scattering mobility,
T = temperature in degrees Kelvin,
k = Boltzmann constant,
κ = dielectric constant,
m_n, m_p = electron and hole effective mass,
m = electron rest mass,
$\hbar$ = Planck's constant/2π,
E_G = intrinsic ionization energy in electron volts,
β = temperature coefficient of E_G in ev /degree.

4. CONDUCTIVITY FROM 250 TO 500°K

In this section an empirical expression for carrier concentration is determined using conductivity and lattice-scattering mobility. The measurements to be described were made on samples of such purity that impurity scattering was negligible above ~100°. Analysis of the conductivity is restricted here to the range below 500° where extrapolated empirical results only are used. Above 500° the analysis depends upon extrapolated empirical results and theory. Another empirical expression for carrier concentration has been determined from conductivity and mobility.[3] The determination, however, made use of early values of drift mobility and assumed lattice scattering to have a temperature dependence of $T^{-1.5}$. The expression to be obtained in this paper is significantly different from the old one because recent mobility values are higher at room temperature, and it is known that the temperature dependence of lattice-scattering mobility departs from the $T^{-1.5}$ law.

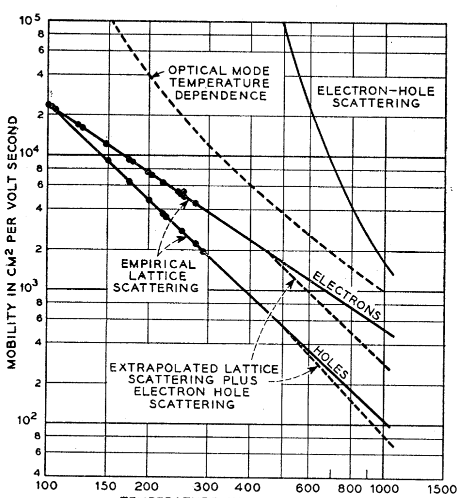

FIG. 1. Conductivity mobility *vs* temperature.

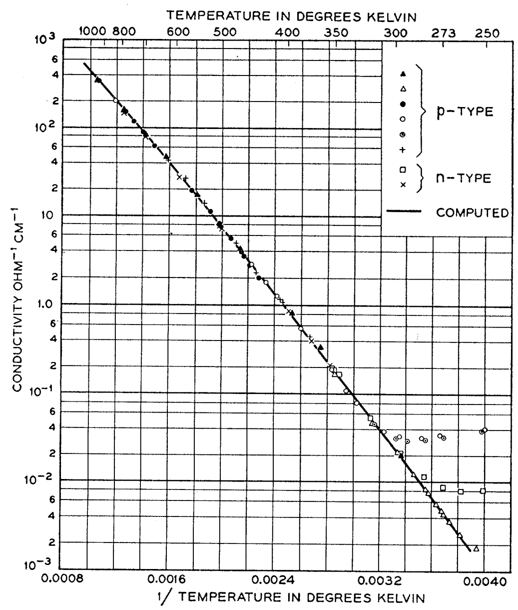

FIG. 2. Conductivity *vs* reciprocal temperature.

4.1 LATTICE-SCATTERING MOBILITY

Theory predicts for lattice scattering by acoustical modes:

$$\mu_{ac} = AT^{-1.5}, \tag{1}$$

and for lattice scattering by optical modes:

$$\mu_{op} = BT^{-0.5}(e^{\Theta/T} - 1), \tag{2}$$

where A, B, and Θ are constants. Lattice-scattering mobility has been determined[1] between 100° and 300°K and the temperature dependence of mobility found to be $T^{-1.66}$ for electrons and $T^{-2.33}$ for holes. These results are shown as plotted points in Fig. 1. For comparison the temperature dependence of μ_{op} is also shown in Fig. 1. This has been computed using $\Theta = 520°$ as determined by Shockley.[4] An absolute value for μ_{op} is not given because the value for B is unknown. It is probable, however, that optical mode scattering is comparable with acoustical mode scattering at temperatures as high as 1000°. Therefore, since the curves for μ_{op} and μ_{ac} do not diverge rapidly with decreasing temperature, it is also probable that optical modes make an appreciable contribution to the scattering over the temperature range where lattice-scattering mobility has been measured. If it is assumed that the departure from the $T^{-1.5}$ law found for electrons is due to an optical mode contribution, the two scattering processes are separable. Lattice-scattering mobility is given approximately by

$$\mu_L^{-1} = \mu_{ac}^{-1} + \mu_{op}^{-1}. \tag{3}$$

When Eqs. (1), (2), and (3) are combined and measured values of μ_L and T inserted, the constants A and B

[3] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72–80 (1950).

[4] W. Shockley, Bell System Tech. J. **30**, 1025 (1951).

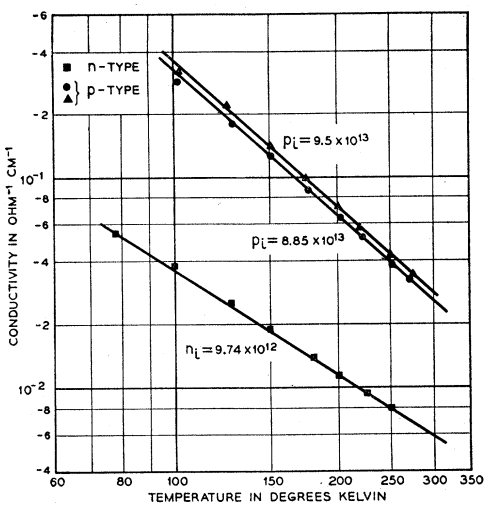

FIG. 3. Conductivity *vs* temperature in the range where carrier concentration is constant.

can be evaluated by solving two simultaneous equations. The results for electrons are

$$\mu_{ac} = 2.4 \times 10^7 T^{-1.5}, \tag{4}$$

$$\mu_{op} = 7.8 \times 10^4 T^{-0.5}(e^{520/T} - 1). \tag{5}$$

These equations generate μ_L *vs* T which coincides with measured μ_L to within the experimental error of ~ 2 percent. This is because so small a contribution from μ_{op} is required to go from $T^{-1.5}$ to $T^{-1.66}$ that the curvature in the μ_{op} temperature dependence (see Fig. 1) does not appear in measured μ_L. However, the contribution from μ_{op} required to go from $T^{-1.5}$ to $T^{-2.33}$ found for holes is so large that the curvature becomes evident and computed μ_{op} differs from measured μ_{op} by 6 percent at 200°. Assuming the maximum contribution by optical modes possible within the 2 percent experimental error leads to the following results for holes:

$$\mu_{ac} = 2.5 \times 10^8 T^{-2.0}, \tag{6}$$

$$\mu_{op} = 1.9 \times 10^4 T^{-0.5}(e^{520/T} - 1). \tag{7}$$

The departure from the $T^{-1.5}$ law shown by Eq. (6) may be due to the location of the valence band at some point other than the center of the Brillouin zone.

The results obtained by this analysis are highly speculative. Furthermore, mobility predicted for the range 300° to 1000° by Eqs. (3), (4), (5), (6), and (7) does not differ importantly from the straight line extrapolation of measured mobility shown in Fig. 1. Therefore, for the purpose of analyzing conductivity and Hall effect, lattice-scattering mobility is taken to be that given by the solid lines of Fig. 1 which represent the equations

$$\mu_{Ln} = 4.90 \times 10^7 T^{-1.66}, \tag{8}$$

$$\mu_{Lp} = 1.05 \times 10^9 T^{-2.33}. \tag{9}$$

4.2 CARRIER CONCENTRATION FROM 250 to 500°K

Conductivity for a number of samples is shown in Fig. 2. At low temperatures the conductivity extends into a range which contains both impurity and intrinsic conductivity. In determining carrier concentration here two procedures are used. Where impurity conductivity is negligible carrier concentration is determined from conductivity and lattice-scattering mobility using Eqs. (8) and (9) and the equation

$$\sigma = e(\mu_{Ln} n + \mu_{Ln} p) = e(np)^{1/2}(\mu_{Ln} + \mu_{Lp}). \tag{10}$$

Where impurity conductivity is important two additional equations are necessary:

$$n = n_i + p \quad \text{for } n\text{-type samples,}$$

$$p = p_i + n \quad \text{for } p\text{-type samples.} \tag{11}$$

The values for n_i and p_i are determined from latttice-scattering mobility and conductivity measured in the range where impurity centers are all ionized. Conductivity in this range is shown for some samples in Fig. 3. The lines drawn through the measured points represent the product

$$e\mu_L n_i (\text{or } p_i).$$

Carrier concentration has been computed as described using Eqs. (8), (9), (10), and (11) in the 250–500° range and is shown as plotted points in Fig. 4. The best fit to these points gives the empirical expression for carrier concentration in the 250–500° range

$$np = 3.10 \times 10^{32} T^3 \exp(-0.785/kT). \tag{12}$$

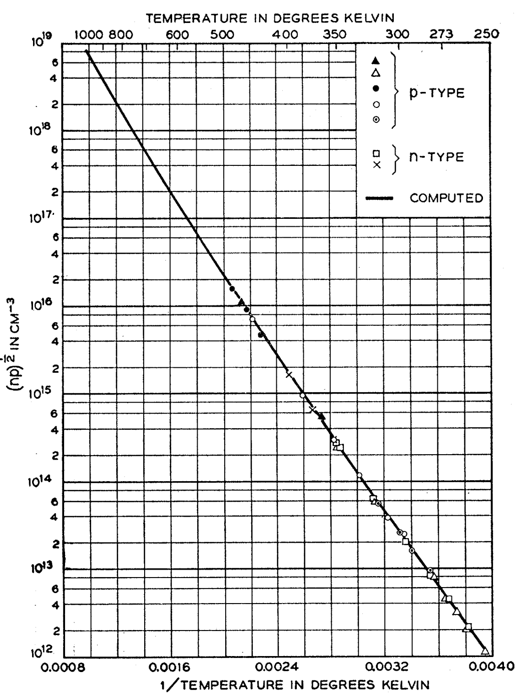

FIG. 4. Square root of the product of electron and hole concentration *vs* reciprocal temperature.

This differs from the old relation[3] in both the constant coefficient and the exponential term. The value of 0.785 is the width of the forbidden gap at $T=0$. The assumption that $\mu_L \propto T^{-1.5}$ made in obtaining the old relation led to a gap width of 0.75 at $T=0$. From lattice-scattering mobility and carrier concentration between 250 to 500° the intrinsic conductivity has been computed and is shown as the solid line in Fig. 2. Equation (12) gives the carrier concentration up to 500° shown as the solid line in Fig. 4.

5. CONDUCTIVITY FROM 500 TO 1000°K

The conductivity obtained from Eqs. (8), (9), and (12) is a factor of 1.30 higher than measured conductivity at 1000°. Above 500° the difference between measured and predicted conductivity increases with increasing temperature at a rate which is much too high to be explained on the basis of optical mode scattering. These results led Shockley to suggest that electron-hole scattering might become effective in reducing mobility when carrier concentration becomes large enough. It was also suggested by Herring that at high carrier concentration the electrostatic interaction of carriers would effectively decrease the intrinsic ionization energy and, therefore, increase the carrier concentration above that predicted by Eq. (12). Consequently, conductivity from 500 to 1000° is computed from mobility adjusted for electron-hole scattering and from carrier concentration adjusted for electrostatic interaction of the carriers. Conductivity computed in this way is to be compared with measured conductivity.

5.1 ELECTRON-HOLE SCATTERING MOBILITY

Electron-hole scattering mobility has been computed using the modified impurity-scattering formula of Conwell, Weisskopf, Brooks, and Herring[2] in the form

$$\mu_{np}=2^{7/2}\kappa^2(kT)^{3/2}/\pi^{3/2}(m_n m_p/[m_n+m_p])^{1/2} \times e^3(np)^{1/2}[\ln(1+B)-B/(1+B)],$$

$$B=6\kappa(m_n m_p/[m_n+m_p])k^2T^2/(np)^{1/2}\hbar^2e^2.$$

Evaluating this gives

$$\mu_{np}=8.5\times10^{17}T^{3/2}(m/m_n+m/m_p)^{1/2}/(np)^{1/2} \times[\ln(1+B)-B(1+B)], \quad (13)$$

$$B=2.07\times10^{15}T^2/(np)^{1/2}(m/m_n+m/m_p).$$

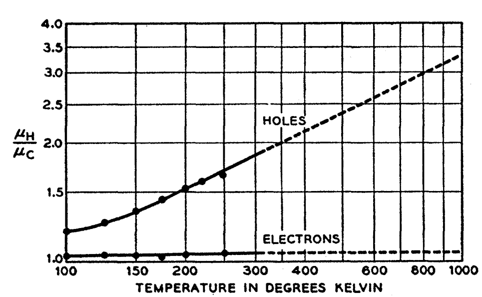

FIG. 5. Hall mobility/conductivity mobility *vs* temperature.

In computing μ_{np}, inertial masses measured by Benedict and Shockley have been used, $m_n=0.6m$,[5] and $m_p=0.3m$.[6] The computed μ_{np} is shown in Fig. 1. It is combined with μ_{Ln} and μ_{Lp} by using the method for combining μ_L and impurity-scattering mobility described by Debye and Conwell.[2] The resulting mobility is shown in Fig. 1 as the dotted line below extrapolated lattice-scattering mobility. Electron-hole scattering decreases the sum of electron and hole mobilities by a factor of 0.60 at 1000°K.

5.2 ELECTROSTATIC INTERACTION OF CARRIERS

In computing carrier concentration above 500° from Eq. (12), a correction to (12) must be made to include the decrease in forbidden gap due to electrostatic

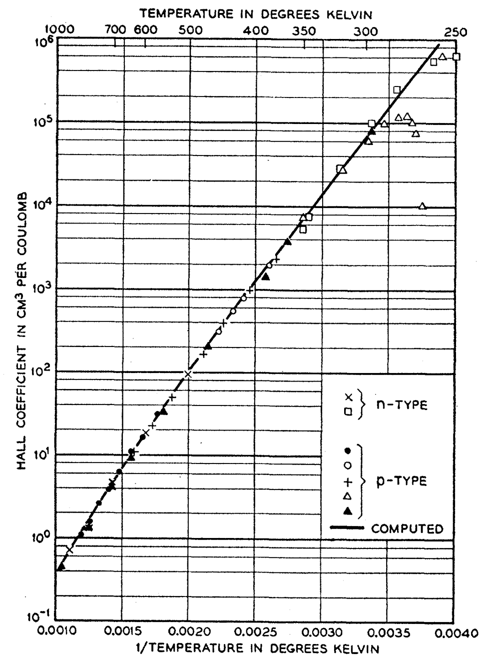

FIG. 6. Hall coefficient *vs* reciprocal temperature.

interaction of carriers. This correction,[7] as suggested by Herring and given in terms of the change in electrochemical potential of the carriers, is

$$\Delta\bar{\mu}=-(e^2/2\kappa)[4\pi e^2(n+p)/\kappa kT]^{1/2},$$

and

$$\Delta E_G=\Delta\bar{\mu}\text{ (for electrons)}+\Delta\bar{\mu}\text{ (for holes)}.$$

Evaluating:

$$\Delta E_G=-4.61\times10^{-10}(np)^{1/4}T^{-1/2}. \quad (14)$$

By use of Eqs. (12) and (14), $(np)^{1/2}$ has been computed and is shown in Fig. 4. The electrostatic interaction

[5] T. S. Benedict and W. Shockley, Phys. Rev. **89**, 1152 (1953).
[6] T. S. Benedict, Phys. Rev. **91**, 1565 (1953).
[7] See, for example, the Debye-Hückel theory in W. J. Moore, *Physical Chemistry* (Prentice-Hall, Inc., New York, 1950), p. 447.

increases carrier concentration at 1000° by a factor of 1.25 over that predicted by (12).

Using mobility determined in Sec. 5.1 and carrier concentration determined in Sec. 5.2, conductivity has been computed from 500 to 1000°K and is shown in Fig. 2. The agreement between measured and computed conductivity is surprisingly good.

6. HALL EFFECT

Hall effect in the intrinsic range is given by the expression[8]

$$R_H=(np)^{1/2}e[-\mu_{cn}{}^2(\mu_{Hn}/\mu_{cn})+\mu_{cp}{}^2(\mu_{Hp}/\mu_{cp})]/\sigma^2. \quad (15)$$

All of the terms in this expression have been evaluated over the range 250–1000° except the ratio of Hall mobility to conductivity mobility μ_H/μ_c. The conductivity mobility is that obtained in Sec. 5.1 and used to compute σ and is written as μ_c in expression (12) to distinguish it from Hall mobility μ_H. The mobility ratio has been determined[1] up to 250° and is shown as plotted points in Fig. 5. The values of μ_H/μ_c used to compute R_H are shown in Fig. 5 as a dashed extrapolation of the measured values. Hall coefficient has been computed using Eq. (15) and is shown compared to measured R_H in Fig. 6. The agreement between experiment and theory is very good but may be accidental. According to Herring, theory suggests that μ_H/μ_c for holes decreases at high temperature to some constant value rather than increasing as assumed in the extrapolation.

7. TEMPERATURE DEPENDENCE OF E_G

The theoretical formula for carrier concentration in the intrinsic range can be written

$$np=2.33\times10^{31}(m_nm_p/m^2)^{3/2}T^3\exp-E_G/kT. \quad (16)$$

This equation has the same form as empirical Eq. (12), but the numerical factor in (12) is larger than the theoretical value by a factor of 13.3 if we assume that effective mass equals rest mass. This can be explained as resulting from a change in E_G with temperature. If a linear variation is assumed,

$$E_G(T)=E_G(0)-\beta T. \quad (17)$$

Then $\beta=k\ln13.3=2.23\times10^{-4}$ ev/degree for $m_nm_p/m^2=1$. Bardeen and Shockley[3] find $\beta=1\times10^{-4}$ by this method. The different result is to be expected because the carrier concentration used by Bardeen and Shockley depended upon early drift mobility measurements and the assumption that $\mu_c\propto T^{-1.5}$.

At the present time, the values of m_n and m_p are uncertain. From thermoelectric effect measurements Geballe[9] finds $m_n=m_p=0.6m$ for the mass parameters in Eq. (16). From the assumption $m_n=m_p=0.6m$,

$$\beta=k\ln13.3\times4.6=3.5\times10^{-4}\text{ ev/degree.}$$

$E_G(0)$ was found in Sec. 4.2 to be 0.785 ev.

Equation (17) must be modified above $T=500°$ to include the effect on E_G by the electrostatic interaction of charge carriers. This can be done by combining (14), (17), and the results above to give

$$E_G=0.785-3.5\times10^{-4}T-4.61\times10^{-10}(np)^{1/4}T^{-1/2}. \quad (18)$$

E_G computed from (18) is shown in Fig. 7.

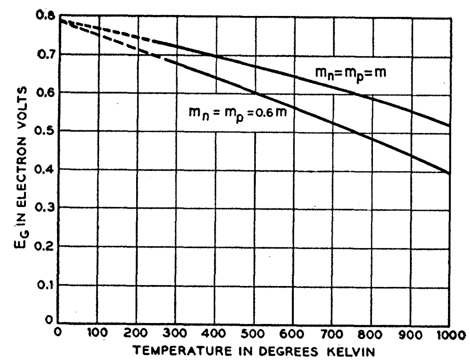

FIG. 7. Intrinsic ionization energy *vs* temperature.

8. SUMMARY

Conductivity and Hall effect have been measured in the intrinsic range of germanium and the results are compared with theory. Agreement between experiment and theory is good.

Conductivity is computed from theory with the following assumptions:

1. The empirical behavior of lattice-scattering mobility as determined between 100–300° can be extrapolated to 1000°.
2. Scattering by electron-hole collisions is important and is given by an impurity-scattering formula with carrier concentration substituted for impurity concentration and a reduced inertial mass substituted for carrier mass.
3. Carrier concentration is given by an empirical formula determined below 500°K from conductivity and lattice-scattering mobility and corrected for the change in gap width due to electrostatic interaction of the carriers.

Hall coefficient is computed from theory using the assumptions listed above with the additional assumption of a simple extrapolation of the empirically determined ratio of Hall mobility to conductivity mobility.

[8] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), first edition, p. 279.

[9] T. H. Geballe (to be published).